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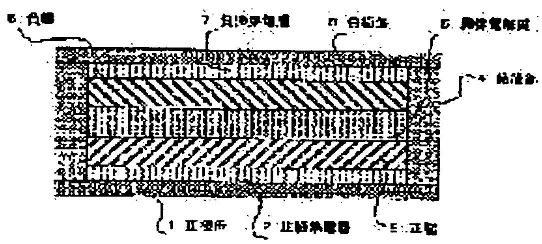
(54) SOLID ELECTROLYTE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To solve problems that the resistance to ionic conduction among particles is high because the contact of crystalline oxide with an active substance that is the same crystalline becomes a point contact, and further, that the internal resistance of solid electrolyte battery which is bonded using amorphous oxide is also high and that the utilization efficiency is inferior.

SOLUTION: In the solid-electrolyte battery in which the solid electrolyte is pinched and retained between a positive electrode and negative electrode that employ an oxide as an active substance in which a reversible occlusion/ emission of lithium ion is possible, particles of the active substance and solid electrolyte are that to which amorphous silica is chemically bonded at the particle face.



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CLAIMS

[Claim(s)]
[Claim 1] It is the solid electrolyte cell characterized by an amorphous silica carrying out the chemical bond of the particle of said active material and a solid electrolyte at the particle front face in the solid electrolyte cell which pinches the solid electrolyte which consists of crystalline substance oxide which has lithium ion conductivity between the positive electrodes and negative electrodes which use as an active material the oxide in which reversible occlusion emission of a lithium ion is possible.
[Claim 2] The solid electrolyte cell according to claim 1 characterized by said active material being at least one kind in a spinel mold lithium manganese multiple oxide, a spinel mold lithium magnesium manganese multiple oxide, a spinel mold lithium nickel manganese multiple oxide, a spinel mold lithium titanium multiple oxide, a spinel mold lithium niobium titanium multiple oxide, and a spinel mold lithium iron titanium multiple oxide.
[Claim 3] Said solid electrolyte Li1+xMxTi2-x(PO4)3[M aluminum or Ga], Li1+x+yMxTi2-xSiyP3-yO12[M aluminum or Ga], Li1+(4-n) xMxTi2-x(PO4)3[-- n[when a univalent or divalent cation and M of M are univalent and n= 1 and M are divalent] = -- the solid electrolyte cell according to claim 1 characterized by 2 and x being at least one kind in 0.1 - 0.5].
[Claim 4] The solid electrolyte cell according to claim 1 characterized by binding the particle of said active material and a solid electrolyte with an amorphous oxide.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the solid electrolyte cell which pinches the solid electrolyte which consists of crystalline substance oxide which has lithium ion conductivity between the positive electrodes and negative electrodes which use as an active material especially the oxide in which reversible occlusion emission of a lithium ion is possible about a solid electrolyte cell.
[0002]
[Description of the Prior Art] With wonderful development of mobile communications in recent years, as a power source of mobile communication equipment, it is small and the need of a lithium secondary battery with a high energy density is increasing rapidly.
[0003] Furthermore, since the energy density of a lithium secondary battery is high, applying to the large-sized cell used for an electric vehicle etc. is also examined.
[0004] However, since the electrolytic solution is used like [a lithium secondary battery] other cells, we are anxious about the liquid spill which is the greatest factor of the trouble about a cell. Especially, in a lithium secondary battery, since the inflammable organic electrolytic solution is used, there is anxiety in respect of safety.
[0005] Then, many attempts which use a solid electrolyte instead of the organic electrolytic solution are made. There is a solid polymer electrolyte which made a giant molecule like polyethylene oxide dissolve lithium salt, such as $LiClO_4$, in one of the solid electrolytes.
[0006] However, the present condition of the thing of level by which practical use is presented with the interfacial resistance of that the ionic conductivity in the inside of giant-molecule bulk is low since movement of a segment is slow at a room temperature, and a giant-molecule solid electrolyte and an electrode active material since a giant-molecule solid electrolyte is large is having not appeared.
[0007] Some approaches for reducing the interfacial resistance of a solid polymer electrolyte and an electrode active material are also proposed. For example, in JP,8-111233,A, it has proposed using for the particle front face of an active material that to which the chemical bond of the both ends or end of a principal chain of a polyether like polyethylene oxide or polypropylene oxide, a poly thioether like a polyphenylene sulfide thioether, or polyacrylate was carried out.
[0008] According to this approach, since a polyether, the poly thioether, or polyacrylate is carrying out the chemical bond on the surface of the active material, compared with the case where an active material, a polyether, the poly thioether, or polyacrylate is only mixed, the lithium ion tends to fall out from the active material front face, and it becomes easy to arrive at an active material front face. Therefore, there is an advantage that interfacial resistance can be reduced. Even if the volume change of the active material accompanying charge and discharge furthermore occurs, since an active material, a polyether, the poly thioether, or polyacrylate is carrying out the chemical bond, both contact does not worsen. Therefore, there is an advantage that it can control that interfacial resistance increases.
[0009] However, by this approach, complicated actuation of returning to combining a polyether, the poly thioether, or polyacrylate at 120 degrees C for 3 hours is required for an active material

front face, and when mass-producing, in order to have to process a lot of active materials, there is a fault that a manufacturing cost becomes high. Moreover, there is a fault that the unreacted part of a polyether, the poly thioether, or polyacrylate causes the active material and side reaction which are oxidation material, and checks a charge-and-discharge reaction. Moreover, under the conditions of returning at 120 degrees C, since side reaction also becomes easy to occur, a result with sufficient repeatability is hard to be obtained.
[0010] In order to control the side reaction of the unreacted part of a macromolecule, and an active material which is not desirable, in JP,9-97616,A, it has proposed carrying out a polymerization in the condition of having made bulking agents, such as titanium oxide, containing. According to this approach, since titanium oxide serves as an alternative catalyst to the polymerization reaction of a macromolecule, side reaction with an active material cannot occur easily, either, therefore there is an advantage that a charge-and-discharge reaction is also hard to be checked.
[0011] However, since this approach suppresses the reaction of an active material and a solid electrolyte, in order that it may reduce the interfacial resistance of an active material and a solid electrolyte, when introducing a chemical bond among both, it cannot be applied. Therefore, although degradation can be prevented, early resistance has not improved at all about a high thing.
[0012] Thus, since the side reaction which is not desirable occurs between a solid polymer electrolyte and an active material, it is difficult to carry out the chemical bond of some macromolecules to an active material, and to reduce interfacial resistance.
[0013] Moreover, since movement of a segment [in / in a giant-molecule solid electrolyte / a room temperature] is slow, an effective means to solve the problem that the ionic conductivity in the inside of giant-molecule bulk is low has not yet appeared.
[0014] On the other hand, some solid electrolytes in the level in which the ionic conductivity in a room temperature rivals 10-4 to ten to 3 S/cm and the organic electrolytic solution are also examined. As such a solid electrolyte, an amorphous sulfide is mentioned, for example. However, the solid electrolyte cell the amorphous sulfide is chemically unstable and using this has not resulted in utilization.
[0015] Some solid electrolytes which are in the level in which the ionic conductivity in a room temperature rivals 10-4 to ten to 3 S/cm and the organic electrolytic solution in a stable inorganic oxide chemically are also examined. As such a solid electrolyte, $Li_{1+x}M_xTi_{2-x}(PO_4)_3$[M has the lithium ion conductivity crystalline substance oxide expressed with aluminum or Ga], for example. Such a lithium ion conductivity crystalline substance oxide is called a common name LISICON, and the presentation and synthetic conditions are studied by many researchers.
[0016] However, since contact to the active material which is similarly a crystalline substance turns into point contact, a crystalline substance oxide has the high resistance to the ionic conduction between particles, and the present condition is that the solid electrolyte cell of the level with which practical use is presented has not yet appeared.
[0017] Then, this invention person etc. found out wholeheartedly becoming the solid electrolyte cell which can operate at a room temperature by binding the particle of the active material of a crystalline substance, and a solid electrolyte with an amorphous oxide as a result of research. It is thought that the hopping site which needs amorphous oxide for lithium ion conduction is offered.
[0018] However, the solid electrolyte cell bound with the amorphous oxide also had high internal resistance, and had the problem that the use effectiveness of an active material was bad.
[0019] this invention person etc. examined the means for [of an active material and a solid electrolyte] making it exist in near very much for the hopping site required for lithium ion conduction by conjecturing the thing resulting from the contact to oxide and an active material with this amorphous cause and contact to amorphous oxide and an amorphous solid electrolyte being inadequate in a molecular level and atomic level, and resulted in this invention.
[0020]
[Means for Solving the Problem] In order to solve the above-mentioned technical problem, according to the solid electrolyte cell concerning this invention, in the solid electrolyte cell which

pinches a solid electrolyte between the positive electrodes and negative electrodes which use as an active material the oxide in which reversible occlusion emission of a lithium ion is possible, the particle of said active material and a solid electrolyte is characterized by an amorphous silica carrying out a chemical bond to the particle front face.

[0021] It is desirable for said active material to be at least one kind in a spinel mold lithium manganese multiple oxide, a spinel mold lithium magnesium manganese multiple oxide, a spinel mold lithium nickel manganese multiple oxide, a spinel mold lithium titanium multiple oxide, a spinel mold lithium niobium titanium multiple oxide, and a spinel mold lithium iron titanium multiple oxide in the above-mentioned solid electrolyte cell.

[0022] In the above-mentioned solid electrolyte cell, said solid electrolyte Li1+xMxTi2-x(PO4)3 [M Moreover, aluminum or Ga], Li1+x+yMxTi2-xSiyP3-yO12[M aluminum or Ga], Li1+(4-n) xMxTi2-x(PO4)3[-- n[when a univalent or divalent cation and M of M are univalent and n= 1 and M are divalent] = -- as for 2 and x, it is desirable that it is at least one kind in 0.1 - 0.5].

[0023] Furthermore, it is desirable to bind the particle of said active material and a solid electrolyte with the above-mentioned solid electrolyte cell with an amorphous oxide.

[0024]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained. the sectional view in which drawing 1 shows the example of a configuration of the solid electrolyte cell of this invention -- it is -- 1 -- a positive-electrode can and 2 -- for the insulating section and 5, as for a negative electrode and 7, a solid electrolyte and 6 are [a positive-electrode current collection layer and 3 / a positive electrode and 4 / a negative-electrode current collection layer and 8] negative-electrode cans.

[0025] As an active material used for a positive electrode 3 and a negative electrode 6, at least one kind in a spinel mold lithium manganese multiple oxide, a spinel mold lithium magnesium manganese multiple oxide, a spinel mold lithium nickel manganese multiple oxide, a spinel mold lithium titanium multiple oxide, a spinel mold lithium niobium titanium multiple oxide, and a spinel mold lithium iron titanium multiple oxide is used. Since it is uninfluential to the ejection and insertion of a lithium ion in which field of a crystal there is no anisotropy, therefore is in contact with the solid electrolyte in order that, as for these, the channel of a lithium ion may take the three-dimensional structure, it is suitable as an active material used for a solid electrolyte cell. Moreover, these active materials have a small volume change accompanying charge and discharge, therefore since the crystal collapse accompanying charge and discharge cannot take place easily, they are suitable as an active material used for a solid electrolyte cell.

[0026] Using bound water and the water of adsorption on the front face of a particle of these active materials, silica raw materials, such as tetra-alkoxysilane, can be combined and the active material particle in which the amorphous silica carried out the chemical bond can be obtained by carrying out the polymerization of the silica raw material further. Association of the silica raw material on the front face of a particle of an active material and the polymerization of silica raw materials are possible only by stirring at a room temperature, and are not accompanied by complicated actuation of a ring current etc. In addition, in order to promote a reaction, water and the acid of a minute amount may be added very much as a catalyst. Thus, since [on the front face of a particle of an active material] it exists even in near very much, the oxide ion used as the hopping site of a lithium ion tends to fall out [the lithium ion] from the active material front face compared with the unsettled active material, and a lithium ion becomes easy to arrive at an active material front face by making the particle front face of an active material carry out the chemical bond of the amorphous silica. Therefore, the interfacial resistance of an active material particle and an amorphous oxide can be reduced. Moreover, even if the volume change of the active material accompanying charge and discharge occurs, since the amorphous silica is carrying out the chemical bond to the active material, both contact does not worsen. Therefore, it can control that interfacial resistance increases. Furthermore, the reaction of an active material and a silica raw material is only dehydration, and other side reaction which checks a charge-and-discharge reaction cannot occur. In addition, in case a cell is formed so that it may mention later, in order to heat-treat above 500 degrees C, dehydration is ended nearly completely and the generated water does not check a charge-and-discharge reaction.

[0027] The active material, amorphous oxide, and shaping assistant to which the chemical bond of the amorphous silica was carried out are mixed. for producing a positive electrode 3 and a negative electrode 6 -- (1) -- After distributing water or an organic solvent, adjusting a slurry, applying this slurry on a base material film and drying, the approach of heat-treating what was judged at 500-800 degrees C, and (2) -- the active material and amorphous oxide to which the chemical bond of the amorphous silica was carried out After adding and corning a direct or shaping assistant, supplying to metal mold and carrying out pressing with a press machine, After carrying out pressing of the approach of heat-treating at 500-800 degrees C, and the mixture which carried out (3) granulation with a roll press machine and processing it in the shape of a sheet, the approach of cutting out the sheet and heat-treating at 500-800 degrees C etc. is used.
[0028] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.
[0029] As a base material film, resin films, such as polyethylene terephthalate, are usable, for example.
[0030] As a lithium ion conductivity crystalline substance particle used for a solid electrolyte 5 aluminum or Ga], and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$[M $Li_{1+x}M_xTi_{2-x}(PO_4)_3$[M aluminum or Ga], $Li_{1+(4-n)x}M_xTi_{2-x}(PO_4)_3$[-- n[when a univalent or divalent cation and M of M are univalent and n= 1 and M are divalent] = -- as for 2 and x, at least one kind in 0.1 - 0.5] is used.
[0031] Using bound water and the water of adsorption on the front face of a particle of these solid electrolytes, silica raw materials, such as tetra-alkoxysilane, can be combined and the particle of the solid electrolyte in which the amorphous silica carried out the chemical bond can be obtained by carrying out the polymerization of the silica raw material further. Association of the silica raw material on the front face of a particle of a solid electrolyte and the polymerization of silica raw materials are possible only by stirring at a room temperature, and are not accompanied by complicated actuation of a ring current etc. In addition, in order to promote a reaction, water and the acid of a minute amount may be added very much as a catalyst. Thus, since [on the front face of a particle of a solid electrolyte] it exists even in near very much, the oxide ion used as the hopping site of a lithium ion tends to fall out [the lithium ion] from the solid electrolyte front face compared with the unsettled solid electrolyte, and a lithium ion becomes easy to arrive at a solid electrolyte front face by making the particle front face of a solid electrolyte carry out the chemical bond of the amorphous silica. Therefore, interfacial resistance can be reduced. Furthermore, the reaction of a solid electrolyte and a silica raw material is only dehydration, and other side reaction which checks a charge-and-discharge reaction cannot occur. In addition, in case a cell is formed so that it may mention later, in order to heat-treat above 500 degrees C, dehydration is ended nearly completely and the generated water does not check a charge-and-discharge reaction.
[0032] The particle, amorphous oxide, and shaping assistant of a solid electrolyte to which the chemical bond of the amorphous silica was carried out are mixed. for producing a solid electrolyte 5 -- (1) -- After distributing water or an organic solvent, adjusting a slurry, applying this slurry on a base material film and drying, the approach of heat-treating what was judged at 500-800 degrees C, and (2) -- the particle and amorphous oxide of a solid electrolyte to which the chemical bond of the amorphous silica was carried out After adding and corning a direct or shaping assistant, supplying to metal mold and carrying out pressing with a press machine, After carrying out pressing of the approach of heat-treating at 500-800 degrees C, and the mixture which carried out (3) granulation with a roll press machine and processing it in the shape of a sheet, the approach of cutting out the sheet and heat-treating at 500-800 degrees C etc. is used.
[0033] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.
[0034] As a base material film, resin films, such as polyethylene terephthalate, are usable, for example.

[0035] As an amorphous oxide used for binding an active material and a lithium ion conductivity crystalline substance particle, 40Li2O-35 B-2O3-25LiNbO3, 30LiI-41Li2O-29P2O5, etc. can be mentioned, for example.
[0036] The positive-electrode current collection layer 2 and the negative-electrode current collection layer 7 consist of the gold which has been arranged for contact to the positive-electrode can 1, a positive electrode 3, or the negative-electrode can 8 and a negative electrode 6, and current collection, for example, was formed of sputtering on the positive electrode 3 and the negative electrode 6, silver, copper, platinum, palladium, nickel, etc.
[0037] The positive-electrode can 1 and the negative-electrode can 8 are arranged in order to prevent a charge-and-discharge reaction being checked by the moisture in atmospheric air, and in order to use as each terminal of a positive electrode 3 and a negative electrode 6, for example, the sheet metal of metals, such as aluminum, copper, nickel, stainless steel, and titanium, is used.
[0038] In order that the insulating section 4 may prevent the short circuit of a positive electrode 3 and a negative electrode 6, it is arranged, for example, macromolecules, such as polyethylene, polypropylene, and polyimide, are used.
[0039]
[Example 1] Li1.1Mn 1.9O4 -- a 100wt(s)% and tetramethoxy silane -- 50wt(s)% -- after carrying out weighing capacity and stirring at a room temperature for 2 hours, Li1.1Mn 1.9O4 to which the chemical bond of the amorphous silica was carried out was obtained by drying at 120 degrees C for 2 hours.
[0040] Li1.1Mn 1.9O4 to which the chemical bond of the amorphous silica was carried out -- 95wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 5wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it.
[0041] The positive-electrode tape and the negative-electrode tape were produced with the doctor blade method using this slurry. In addition, in a negative electrode, 3V charge-and-discharge field of Li1.1Mn 1.9O4 is used.
[0042] Li1.3aluminum0.3Ti1.7(PO4) 3 [next,] -- a 100wt(s)% and tetramethoxy silane -- 50wt (s)% -- after carrying out weighing capacity and stirring at a room temperature for 2 hours, Li1.3aluminum0.3Ti1.7(PO4) 3 to which the chemical bond of the amorphous silica was carried out were obtained by drying at 120 degrees C for 2 hours.
[0043] Li1.3aluminum0.3Ti1.7(PO4) 3 to which the chemical bond of the amorphous silica was carried out -- 90wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 10wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it.
[0044] The solid electrolyte tape was fabricated with the doctor blade method using this slurry.
[0045] After carrying out the laminating of a positive-electrode tape, a solid electrolyte tape, and the negative-electrode tape and sticking them by pressure, it heat-treated at 650 degrees C for 3 hours. The size after heat treatment was 30x30mm, and, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of thickness] 100 micrometers 210 micrometers in total.
[0046] After carrying out sputtering of the gold and forming a current collection layer in a positive-electrode and negative-electrode side, it inserted in the polyethylene frame of 31x31mm of insides, and 35x35mm of outsides, and the solid electrolyte cell was produced by inserting and carrying out thermocompression bonding to the aluminum plate of two sheets.
[0047]
[Example 2] Li1.1Mn 1.9O4 -- a 100wt(s)% and tetramethoxy silane -- 50wt(s)% -- after carrying out weighing capacity and stirring at a room temperature for 2 hours, Li1.1Mn 1.9O4 to which the chemical bond of the amorphous silica was carried out was obtained by drying at 120 degrees C for 2 hours.
[0048] Li1.1Mn 1.9O4 to which the chemical bond of the amorphous silica was carried out -- 95wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 5wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in

addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it. The positive-electrode tape was produced with the doctor blade method using this slurry.
[0049] next, Li1.33Ti 1.67O4 -- a 100wt(s)% and tetramethoxy silane -- 50wt(s)% -- after stirring at a room temperature for 2 hours, having carried out weighing capacity and irradiating UV, Li1.33Ti 1.67O4 to which the chemical bond of the amorphous silica was carried out was obtained by drying at 120 degrees C for 2 hours.
[0050] Li1.33Ti 1.67O4 to which the chemical bond of the amorphous silica was carried out -- 95wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 5wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it. The negative-electrode tape was produced with the doctor blade method using this slurry.
[0051] Li1.3aluminum0.3Ti1.7(PO4) 3 [next,] -- a 100wt(s)% and tetramethoxy silane -- 50wt (s)% -- after carrying out weighing capacity and stirring at a room temperature for 2 hours, Li1.3aluminum0.3Ti1.7(PO4) 3 to which the chemical bond of the amorphous silica was carried out were obtained by drying at 120 degrees C for 2 hours.
[0052] Li1.3aluminum0.3Ti1.7(PO4) 3 to which the chemical bond of the amorphous silica was carried out -- 90wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 10wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it. The solid electrolyte tape was fabricated with the doctor blade method using this slurry.
[0053] After carrying out the laminating of a positive-electrode tape, a solid electrolyte tape, and the negative-electrode tape and sticking them by pressure, it heat-treated at 650 degrees C for 3 hours. The size after heat treatment was 30x30mm, and, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of thickness] 100 micrometers 210 micrometers in total.
[0054] After carrying out sputtering of the gold and forming a current collection layer in a positive-electrode and negative-electrode side, it inserted in the polyethylene frame of 31x31mm of insides, and 35x35mm of outsides, and the solid electrolyte cell was produced by inserting and carrying out thermocompression bonding to the aluminum plate of two sheets.
[0055]
[The example 1 of a comparison] When removing not processing the particle of an active material and a solid electrolyte by the tetramethoxy silane, the solid electrolyte cell was produced by the same approach as an example 1.
[0056]
[The example 2 of a comparison] When removing not processing the particle of an active material and a solid electrolyte by the tetramethoxy silane, the solid electrolyte cell was produced by the same approach as an example 2.
[0057]
[Electrochemical evaluation] Charge-and-discharge capacity was measured with the current density of 100microA/cm2 using the above solid electrolyte cell. The result is shown in Table 1.
[0058]
[Table 1]

試　料	充電容量 (mAh/g)	放電容量 (mAh/g)	充放電効率 (%)
実施例1	105	91	87
実施例2	99	86	87
比較例1	80	36	45
比較例2	82	40	49

[0059] As shown in Table 1, in the examples 1 and 2 using the particle of the active material to which it processed by the tetramethoxy silane and the chemical bond of the amorphous silica was carried out, and a solid electrolyte, compared with the examples 1 and 2 of a comparison using the particle of an unsettled active material and a solid electrolyte, an early charge capacity

is high, and charge-and-discharge effectiveness is high.
[0060] When the amorphous silica carried out the chemical bond of this to the particle front face of an active material and a solid electrolyte, since it exists even in near very much, and the oxide ion used as the hopping site of a lithium ion reduced interfacial resistance compared with the particle of an unsettled active material and a solid electrolyte, it is guessed on the front face of a particle of an active material and a solid electrolyte.
[0061]
[Effect of the Invention] According to the solid electrolyte cell concerning this invention, the oxide in which reversible occlusion emission of a lithium ion is possible as mentioned above, between the positive electrodes and negative electrodes which are used as an active material In the solid electrolyte cell which pinches the solid electrolyte which consists of a crystalline substance oxide which has lithium ion conductivity From a silica with the particle of the above-mentioned active material and a solid electrolyte amorphous on the particle front face carrying out a chemical bond Since [on the front face of a particle of an active material and a solid electrolyte] it exists even in near very much, interfacial resistance is reduced compared with the particle of an unsettled active material and a solid electrolyte, and the oxide ion used as the hopping site of a lithium ion can obtain a solid electrolyte cell with the high use effectiveness of an active material.
[0062] Moreover, even if the volume change of the active material accompanying charge and discharge occurs, since the amorphous silica is carrying out the chemical bond to the active material, both contact does not worsen. Therefore, it can control that interfacial resistance increases. Thereby, early charge-and-discharge effectiveness improves.
[0063] Furthermore, the reaction of an active material or a solid electrolyte, and a silica raw material is only dehydration, and other side reaction which checks a charge-and-discharge reaction cannot occur. Therefore, a result with sufficient repeatability can be obtained.
[0064] In addition, in case a cell is formed, in order to heat-treat above 500 degrees C, dehydration is ended nearly completely and the generated water does not check a charge-and-discharge reaction.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the solid electrolyte cell which pinches the solid electrolyte which consists of crystalline substance oxide which has lithium ion conductivity between the positive electrodes and negative electrodes which use as an active material especially the oxide in which reversible occlusion emission of a lithium ion is possible about a solid electrolyte cell.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] According to the solid electrolyte cell concerning this invention, the oxide in which reversible occlusion emission of a lithium ion is possible as mentioned above, between the positive electrodes and negative electrodes which are used as an active material In the solid electrolyte cell which pinches the solid electrolyte which consists of a crystalline substance oxide which has lithium ion conductivity From a silica with the particle of the above-mentioned active material and a solid electrolyte amorphous on the particle front face carrying out a chemical bond Since [on the front face of a particle of an active material and a solid electrolyte] it exists even in near very much, interfacial resistance is reduced compared with the particle of an unsettled active material and a solid electrolyte, and the oxide ion used as the hopping site of a lithium ion can obtain a solid electrolyte cell with the high use effectiveness of an active material.
[0062] Moreover, even if the volume change of the active material accompanying charge and discharge occurs, since the amorphous silica is carrying out the chemical bond to the active material, both contact does not worsen. Therefore, it can control that interfacial resistance increases. Thereby, early charge-and-discharge effectiveness improves.
[0063] Furthermore, the reaction of an active material or a solid electrolyte, and a silica raw material is only dehydration, and other side reaction which checks a charge-and-discharge reaction cannot occur. Therefore, a result with sufficient repeatability can be obtained.
[0064] In addition, in case a cell is formed, in order to heat-treat above 500 degrees C, dehydration is ended nearly completely and the generated water does not check a charge-and-discharge reaction.

[Translation done.]

TECHNICAL PROBLEM

[Description of the Prior Art] With wonderful development of mobile communications in recent years, as a power source of mobile communication equipment, it is small and the need of a lithium secondary battery with a high energy density is increasing rapidly.
[0003] Furthermore, since the energy density of a lithium secondary battery is high, applying to the large-sized cell used for an electric vehicle etc. is also examined.
[0004] However, since the electrolytic solution is used like [a lithium secondary battery] other cells, we are anxious about the liquid spill which is the greatest factor of the trouble about a cell. Especially, in a lithium secondary battery, since the inflammable organic electrolytic solution is used, there is anxiety in respect of safety.
[0005] Then, many attempts which use a solid electrolyte instead of the organic electrolytic solution are made. There is a solid polymer electrolyte which made a giant molecule like polyethylene oxide dissolve lithium salt, such as $LiClO_4$, in one of the solid electrolytes.
[0006] However, the present condition of the thing of level by which practical use is presented with the interfacial resistance of that the ionic conductivity in the inside of giant-molecule bulk is low since movement of a segment is slow at a room temperature, and a giant-molecule solid electrolyte and an electrode active material since a giant-molecule solid electrolyte is large is having not appeared.
[0007] Some approaches for reducing the interfacial resistance of a solid polymer electrolyte and an electrode active material are also proposed. For example, in JP,8-111233,A, it has proposed using for the particle front face of an active material that to which the chemical bond of the both ends or end of a principal chain of a polyether like polyethylene oxide or polypropylene oxide, a poly thioether like a polyphenylene sulfide thioether, or polyacrylate was carried out.
[0008] According to this approach, since a polyether, the poly thioether, or polyacrylate is carrying out the chemical bond on the surface of the active material, compared with the case where an active material, a polyether, the poly thioether, or polyacrylate is only mixed, the lithium ion tends to fall out from the active material front face, and it becomes easy to arrive at an active material front face. Therefore, there is an advantage that interfacial resistance can be reduced. Even if the volume change of the active material accompanying charge and discharge furthermore occurs, since an active material, a polyether, the poly thioether, or polyacrylate is carrying out the chemical bond, both contact does not worsen. Therefore, there is an advantage that it can control that interfacial resistance increases.
[0009] However, by this approach, complicated actuation of returning to combining a polyether, the poly thioether, or polyacrylate at 120 degrees C for 3 hours is required for an active material front face, and when mass-producing, in order to have to process a lot of active materials, there is a fault that a manufacturing cost becomes high. Moreover, there is a fault that the unreacted part of a polyether, the poly thioether, or polyacrylate causes the active material and side reaction which are oxidation material, and checks a charge-and-discharge reaction. Moreover, under the conditions of returning at 120 degrees C, since side reaction also becomes easy to occur, a result with sufficient repeatability is hard to be obtained.
[0010] In order to control the side reaction of the unreacted part of a macromolecule, and an active material which is not desirable, in JP,9-97616,A, it has proposed carrying out a

polymerization in the condition of having made bulking agents, such as titanium oxide, containing. According to this approach, since titanium oxide serves as an alternative catalyst to the polymerization reaction of a macromolecule, side reaction with an active material cannot occur easily, either, therefore there is an advantage that a charge-and-discharge reaction is also hard to be checked.

[0011] However, since this approach suppresses the reaction of an active material and a solid electrolyte, in order that it may reduce the interfacial resistance of an active material and a solid electrolyte, when introducing a chemical bond among both, it cannot be applied. Therefore, although degradation can be prevented, early resistance has not improved at all about a high thing.

[0012] Thus, since the side reaction which is not desirable occurs between a solid polymer electrolyte and an active material, it is difficult to carry out the chemical bond of some macromolecules to an active material, and to reduce interfacial resistance.

[0013] Moreover, since movement of a segment [in / in a giant-molecule solid electrolyte / a room temperature] is slow, an effective means to solve the problem that the ionic conductivity in the inside of giant-molecule bulk is low has not yet appeared.

[0014] On the other hand, some solid electrolytes in the level in which the ionic conductivity in a room temperature rivals 10-4 to ten to 3 S/cm and the organic electrolytic solution are also examined. As such a solid electrolyte, an amorphous sulfide is mentioned, for example. However, the solid electrolyte cell the amorphous sulfide is chemically unstable and using this has not resulted in utilization.

[0015] Some solid electrolytes which are in the level in which the ionic conductivity in a room temperature rivals 10-4 to ten to 3 S/cm and the organic electrolytic solution in a stable inorganic oxide chemically are also examined. As such a solid electrolyte, Li1+xMxTi2-x(PO4)3[M has the lithium ion conductivity crystalline substance oxide expressed with aluminum or Ga], for example. Such a lithium ion conductivity crystalline substance oxide is called a common name LISICON, and the presentation and synthetic conditions are studied by many researchers.

[0016] However, since contact to the active material which is similarly a crystalline substance turns into point contact, a crystalline substance oxide has the high resistance to the ionic conduction between particles, and the present condition is that the solid electrolyte cell of the level with which practical use is presented has not yet appeared.

[0017] Then, this invention person etc. found out wholeheartedly becoming the solid electrolyte cell which can operate at a room temperature by binding the particle of the active material of a crystalline substance, and a solid electrolyte with an amorphous oxide as a result of research. It is thought that the hopping site which needs amorphous oxide for lithium ion conduction is offered.

[0018] However, the solid electrolyte cell bound with the amorphous oxide also had high internal resistance, and had the problem that the use effectiveness of an active material was bad.

[0019] this invention person etc. examined the means for [of an active material and a solid electrolyte] making it exist in near very much for the hopping site required for lithium ion conduction by conjecturing the thing resulting from the contact to oxide and an active material with this amorphous cause and contact to amorphous oxide and an amorphous solid electrolyte being inadequate in a molecular level and atomic level, and resulted in this invention.

[Translation done.]

MEANS

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, according to the solid electrolyte cell concerning this invention, in the solid electrolyte cell which pinches a solid electrolyte between the positive electrodes and negative electrodes which use as an active material the oxide in which reversible occlusion emission of a lithium ion is possible, the particle of said active material and a solid electrolyte is characterized by an amorphous silica carrying out a chemical bond to the particle front face.
[0021] It is desirable for said active material to be at least one kind in a spinel mold lithium manganese multiple oxide, a spinel mold lithium magnesium manganese multiple oxide, a spinel mold lithium nickel manganese multiple oxide, a spinel mold lithium titanium multiple oxide, a spinel mold lithium niobium titanium multiple oxide, and a spinel mold lithium iron titanium multiple oxide in the above-mentioned solid electrolyte cell.
[0022] In the above-mentioned solid electrolyte cell, said solid electrolyte Li1+xMxTi2-x(PO4)3 [M Moreover, aluminum or Ga], Li1+x+yMxTi2-xSiyP3-yO12[M aluminum or Ga], Li1+(4-n) xMxTi2-x(PO4)3[-- n[when a univalent or divalent cation and M of M are univalent and n= 1 and M are divalent] = -- as for 2 and x, it is desirable that it is at least one kind in 0.1 - 0.5].
[0023] Furthermore, it is desirable to bind the particle of said active material and a solid electrolyte with the above-mentioned solid electrolyte cell with an amorphous oxide.
[0024]
[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained. the sectional view in which drawing 1 shows the example of a configuration of the solid electrolyte cell of this invention -- it is -- 1 -- a positive-electrode can and 2 -- for the insulating section and 5, as for a negative electrode and 7, a solid electrolyte and 6 are [a positive-electrode current collection layer and 3 / a positive electrode and 4 / a negative-electrode current collection layer and 8] negative-electrode cans.
[0025] As an active material used for a positive electrode 3 and a negative electrode 6, at least one kind in a spinel mold lithium manganese multiple oxide, a spinel mold lithium magnesium manganese multiple oxide, a spinel mold lithium nickel manganese multiple oxide, a spinel mold lithium titanium multiple oxide, a spinel mold lithium niobium titanium multiple oxide, and a spinel mold lithium iron titanium multiple oxide is used. Since it is uninfluential to the ejection and insertion of a lithium ion in which field of a crystal there is no anisotropy, therefore is in contact with the solid electrolyte in order that, as for these, the channel of a lithium ion may take the three-dimensional structure, it is suitable as an active material used for a solid electrolyte cell. Moreover, these active materials have a small volume change accompanying charge and discharge, therefore since the crystal collapse accompanying charge and discharge cannot take place easily, they are suitable as an active material used for a solid electrolyte cell.
[0026] Using bound water and the water of adsorption on the front face of a particle of these active materials, silica raw materials, such as tetra-alkoxysilane, can be combined and the active material particle in which the amorphous silica carried out the chemical bond can be obtained by carrying out the polymerization of the silica raw material further. Association of the silica raw material on the front face of a particle of an active material and the polymerization of silica raw materials are possible only by stirring at a room temperature, and are not accompanied by

complicated actuation of a ring current etc. In addition, in order to promote a reaction, water and the acid of a minute amount may be added very much as a catalyst. Thus, since [on the front face of a particle of an active material] it exists even in near very much, the oxide ion used as the hopping site of a lithium ion tends to fall out [the lithium ion] from the active material front face compared with the unsettled active material, and a lithium ion becomes easy to arrive at an active material front face by making the particle front face of an active material carry out the chemical bond of the amorphous silica. Therefore, the interfacial resistance of an active material particle and an amorphous oxide can be reduced. Moreover, even if the volume change of the active material accompanying charge and discharge occurs, since the amorphous silica is carrying out the chemical bond to the active material, both contact does not worsen. Therefore, it can control that interfacial resistance increases. Furthermore, the reaction of an active material and a silica raw material is only dehydration, and other side reaction which checks a charge-and-discharge reaction cannot occur. In addition, in case a cell is formed so that it may mention later, in order to heat-treat above 500 degrees C, dehydration is ended nearly completely and the generated water does not check a charge-and-discharge reaction.
[0027] The active material, amorphous oxide, and shaping assistant to which the chemical bond of the amorphous silica was carried out are mixed. for producing a positive electrode 3 and a negative electrode 6 -- (1) -- After distributing water or an organic solvent, adjusting a slurry, applying this slurry on a base material film and drying, the approach of heat-treating what was judged at 500-800 degrees C, and (2) -- the active material and amorphous oxide to which the chemical bond of the amorphous silica was carried out After adding and corning a direct or shaping assistant, supplying to metal mold and carrying out pressing with a press machine, After carrying out pressing of the approach of heat-treating at 500-800 degrees C, and the mixture which carried out (3) granulation with a roll press machine and processing it in the shape of a sheet, the approach of cutting out the sheet and heat-treating at 500-800 degrees C etc. is used.
[0028] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.
[0029] As a base material film, resin films, such as polyethylene terephthalate, are usable, for example.
[0030] As a lithium ion conductivity crystalline substance particle used for a solid electrolyte 5 aluminum or Ga], and $Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$[M $Li_{1+x}M_xTi_{2-x}(PO_4)_3$[M aluminum or Ga], $Li_{1+(4-n)x}M_xTi_{2-x}(PO_4)_3$[-- n[when a univalent or divalent cation and M of M are univalent and n= 1 and M are divalent] = -- as for 2 and x, at least one kind in 0.1 - 0.5] is used.
[0031] Using bound water and the water of adsorption on the front face of a particle of these solid electrolytes, silica raw materials, such as tetra-alkoxysilane, can be combined and the particle of the solid electrolyte in which the amorphous silica carried out the chemical bond can be obtained by carrying out the polymerization of the silica raw material further. Association of the silica raw material on the front face of a particle of a solid electrolyte and the polymerization of silica raw materials are possible only by stirring at a room temperature, and are not accompanied by complicated actuation of a ring current etc. In addition, in order to promote a reaction, water and the acid of a minute amount may be added very much as a catalyst. Thus, since [on the front face of a particle of a solid electrolyte] it exists even in near very much, the oxide ion used as the hopping site of a lithium ion tends to fall out [the lithium ion] from the solid electrolyte front face compared with the unsettled solid electrolyte, and a lithium ion becomes easy to arrive at a solid electrolyte front face by making the particle front face of a solid electrolyte carry out the chemical bond of the amorphous silica. Therefore, interfacial resistance can be reduced. Furthermore, the reaction of a solid electrolyte and a silica raw material is only dehydration, and other side reaction which checks a charge-and-discharge reaction cannot occur. In addition, in case a cell is formed so that it may mention later, in order to heat-treat above 500 degrees C, dehydration is ended nearly completely and the generated water does not check a charge-and-discharge reaction.
[0032] The particle, amorphous oxide, and shaping assistant of a solid electrolyte to which the

chemical bond of the amorphous silica was carried out are mixed. for producing a solid electrolyte 5 -- (1) -- After distributing water or an organic solvent, adjusting a slurry, applying this slurry on a base material film and drying, the approach of heat-treating what was judged at 500-800 degrees C, and (2) -- the particle and amorphous oxide of a solid electrolyte to which the chemical bond of the amorphous silica was carried out After adding and corning a direct or shaping assistant, supplying to metal mold and carrying out pressing with a press machine, After carrying out pressing of the approach of heat-treating at 500-800 degrees C, and the mixture which carried out (3) granulation with a roll press machine and processing it in the shape of a sheet, the approach of cutting out the sheet and heat-treating at 500-800 degrees C etc. is used.

[0033] As an usable shaping assistant, one sort or two sorts or more of mixture, such as polyacrylic acid, a carboxymethyl cellulose, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, and the poly butyral, is mentioned here, for example.

[0034] As a base material film, resin films, such as polyethylene terephthalate, are usable, for example.

[0035] As an amorphous oxide used for binding an active material and a lithium ion conductivity crystalline substance particle, 40Li2O-35 B-2O3-25LiNbO3, 30LiI-41Li2O-29P2O5, etc. can be mentioned, for example.

[0036] The positive-electrode current collection layer 2 and the negative-electrode current collection layer 7 consist of the gold which has been arranged for contact to the positive-electrode can 1, a positive electrode 3, or the negative-electrode can 8 and a negative electrode 6, and current collection, for example, was formed of sputtering on the positive electrode 3 and the negative electrode 6, silver, copper, platinum, palladium, nickel, etc.

[0037] The positive-electrode can 1 and the negative-electrode can 8 are arranged in order to prevent a charge-and-discharge reaction being checked by the moisture in atmospheric air, and in order to use as each terminal of a positive electrode 3 and a negative electrode 6, for example, the sheet metal of metals, such as aluminum, copper, nickel, stainless steel, and titanium, is used.

[0038] In order that the insulating section 4 may prevent the short circuit of a positive electrode 3 and a negative electrode 6, it is arranged, for example, macromolecules, such as polyethylene, polypropylene, and polyimide, are used.

[0039]

[Example 1] Li1.1Mn 1.9O4 -- a 100wt(s)% and tetramethoxy silane -- 50wt(s)% -- after carrying out weighing capacity and stirring at a room temperature for 2 hours, Li1.1Mn 1.9O4 to which the chemical bond of the amorphous silica was carried out was obtained by drying at 120 degrees C for 2 hours.

[0040] Li1.1Mn 1.9O4 to which the chemical bond of the amorphous silica was carried out -- 95wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 5wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it.

[0041] The positive-electrode tape and the negative-electrode tape were produced with the doctor blade method using this slurry. In addition, in a negative electrode, 3V charge-and-discharge field of Li1.1Mn 1.9O4 is used.

[0042] Li1.3aluminum0.3Ti1.7(PO4) 3 [next,] -- a 100wt(s)% and tetramethoxy silane -- 50wt (s)% -- after carrying out weighing capacity and stirring at a room temperature for 2 hours, Li1.3aluminum0.3Ti1.7(PO4) 3 to which the chemical bond of the amorphous silica was carried out were obtained by drying at 120 degrees C for 2 hours.

[0043] Li1.3aluminum0.3Ti1.7(PO4) 3 to which the chemical bond of the amorphous silica was carried out -- 90wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 10wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it.

[0044] The solid electrolyte tape was fabricated with the doctor blade method using this slurry.

[0045] After carrying out the laminating of a positive-electrode tape, a solid electrolyte tape, and the negative-electrode tape and sticking them by pressure, it heat-treated at 650 degrees C for

3 hours. The size after heat treatment was 30x30mm, and, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of thickness] 100 micrometers 210 micrometers in total.
[0046] After carrying out sputtering of the gold and forming a current collection layer in a positive-electrode and negative-electrode side, it inserted in the polyethylene frame of 31x31mm of insides, and 35x35mm of outsides, and the solid electrolyte cell was produced by inserting and carrying out thermocompression bonding to the aluminum plate of two sheets.
[0047]
[Example 2] Li1.1Mn 1.9O4 -- a 100wt(s)% and tetramethoxy silane -- 50wt(s)% -- after carrying out weighing capacity and stirring at a room temperature for 2 hours, Li1.1Mn 1.9O4 to which the chemical bond of the amorphous silica was carried out was obtained by drying at 120 degrees C for 2 hours.
[0048] Li1.1Mn 1.9O4 to which the chemical bond of the amorphous silica was carried out -- 95wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 5wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it. The positive-electrode tape was produced with the doctor blade method using this slurry.
[0049] next, Li1.33Ti 1.67O4 -- a 100wt(s)% and tetramethoxy silane -- 50wt(s)% -- after stirring at a room temperature for 2 hours, having carried out weighing capacity and irradiating UV, Li1.33Ti 1.67O4 to which the chemical bond of the amorphous silica was carried out was obtained by drying at 120 degrees C for 2 hours.
[0050] Li1.33Ti 1.67O4 to which the chemical bond of the amorphous silica was carried out -- 95wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 5wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it. The negative-electrode tape was produced with the doctor blade method using this slurry.
[0051] Li1.3aluminum0.3Ti1.7(PO4) 3 [next,] -- a 100wt(s)% and tetramethoxy silane -- 50wt(s)% -- after carrying out weighing capacity and stirring at a room temperature for 2 hours, Li1.3aluminum0.3Ti1.7(PO4) 3 to which the chemical bond of the amorphous silica was carried out were obtained by drying at 120 degrees C for 2 hours.
[0052] Li1.3aluminum0.3Ti1.7(PO4) 3 to which the chemical bond of the amorphous silica was carried out -- 90wt(s)% and 40Li2O-35 B-2O3-25LiNbO3 -- 10wt(s)% -- weighing capacity was carried out, the poly butyral was stirred 5wt(s)%, isopropyl alcohol was stirred to this with the 25wt(s)%, in addition planet mold ball mill for 30 minutes, and the slurry was adjusted to it. The solid electrolyte tape was fabricated with the doctor blade method using this slurry.
[0053] After carrying out the laminating of a positive-electrode tape, a solid electrolyte tape, and the negative-electrode tape and sticking them by pressure, it heat-treated at 650 degrees C for 3 hours. The size after heat treatment was 30x30mm, and, for the positive electrode, 100 micrometers and a solid electrolyte were [10 micrometers and the negative electrode of thickness] 100 micrometers 210 micrometers in total.
[0054] After carrying out sputtering of the gold and forming a current collection layer in a positive-electrode and negative-electrode side, it inserted in the polyethylene frame of 31x31mm of insides, and 35x35mm of outsides, and the solid electrolyte cell was produced by inserting and carrying out thermocompression bonding to the aluminum plate of two sheets.
[0055]
[The example 1 of a comparison] When removing not processing the particle of an active material and a solid electrolyte by the tetramethoxy silane, the solid electrolyte cell was produced by the same approach as an example 1.
[0056]
[The example 2 of a comparison] When removing not processing the particle of an active material and a solid electrolyte by the tetramethoxy silane, the solid electrolyte cell was produced by the same approach as an example 2.
[0057]
[Electrochemical evaluation] Charge-and-discharge capacity was measured with the current

density of 100microA/cm2 using the above solid electrolyte cell. The result is shown in Table 1.
[0058]
[Table 1]

試　料	充電容量 (mAh／g)	放電容量 (mAh／g)	充放電効率 (%)
実施例1	105	91	87
実施例2	99	86	87
比較例1	80	36	45
比較例2	82	40	49

[0059] As shown in Table 1, in the examples 1 and 2 using the particle of the active material to which it processed by the tetramethoxy silane and the chemical bond of the amorphous silica was carried out, and a solid electrolyte, compared with the examples 1 and 2 of a comparison using the particle of an unsettled active material and a solid electrolyte, an early charge capacity is high, and charge-and-discharge effectiveness is high.
[0060] When the amorphous silica carried out the chemical bond of this to the particle front face of an active material and a solid electrolyte, since it exists even in near very much, and the oxide ion used as the hopping site of a lithium ion reduced interfacial resistance compared with the particle of an unsettled active material and a solid electrolyte, it is guessed on the front face of a particle of an active material and a solid electrolyte.

[Translation done.]

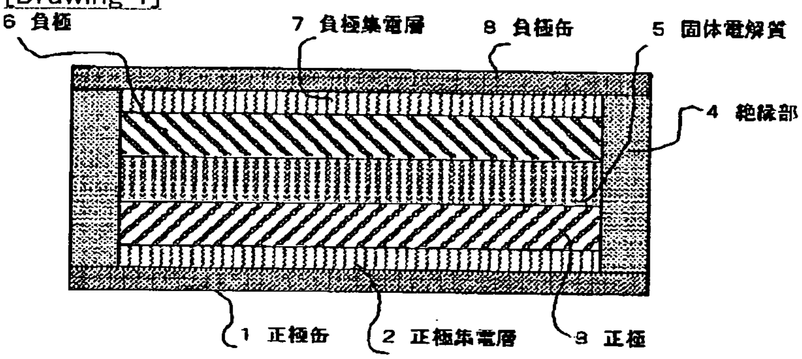
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view showing the example of a configuration of the solid electrolyte cell concerning this invention.
[Description of Notations]
1: A positive-electrode can, 2:positive-electrode current collection layer, 3:positive electrode, 4:insulation section, 5:solid electrolyte, 6:negative electrode, 7:negative-electrode current collection layer, 8 : negative-electrode can

[Translation done.]

DRAWINGS

[Drawing 1]



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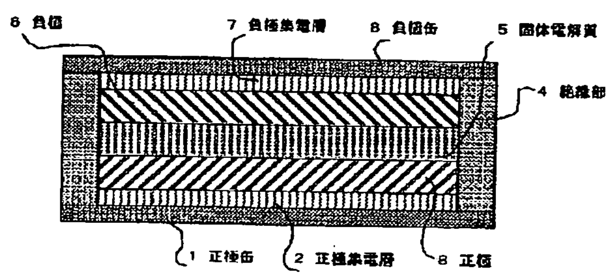
最終頁に続く

(54)【発明の名称】　固体電解質電池

(57)【要約】
【課題】　結晶質酸化物は、同じく結晶質である活物質との接触が点接触になるため、粒子間のイオン伝導に対する抵抗が高いという問題があった。また、非晶質の酸化物で結着した固体電解質電池も、内部抵抗が高く、活物質の利用効率が悪いという問題があった。
【解決手段】　リチウムイオンの可逆的な吸蔵放出が可能な酸化物を活物質とする正極および負極との間に固体電解質を挟持する固体電解質電池において、上記活物質および固体電解質の粒子は、その粒子表面に非晶質のシリカが化学結合したものであることを特徴とする。



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【特許請求の範囲】

【請求項１】　リチウムイオンの可逆的な吸蔵放出が可能な酸化物を活物質とする正極および負極との間に、リチウムイオン伝導性を有する結晶質酸化物からなる固体電解質を挟持する固体電解質電池において、前記活物質および固体電解質の粒子は、その粒子表面に非晶質のシリカが化学結合したものであることを特徴とする固体電解質電池。

【請求項２】　前記活物質がスピネル型リチウムマンガン複合酸化物、スピネル型リチウムマグネシウムマンガン複合酸化物、スピネル型リチウムニッケルマンガン複合酸化物、スピネル型リチウムチタン複合酸化物、スピネル型リチウムニオブチタン複合酸化物、およびスピネル型リチウム鉄チタン複合酸化物のうちの少なくとも１種類であることを特徴とする請求項１に記載の固体電解質電池。

【請求項３】　前記固体電解質が、$Li_{1+x}M_xTi_{2-x}(PO_4)_3$［MはＡｌまたはＧａ］、$Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$［MはＡｌまたはＧａ］、$Li_{1+(4-n)x}M_xTi_{2-x}(PO_4)_3$［Mは１価または２価の陽イオン、Mが１価のときｎ＝１、Mが２価のときｎ＝２、ｘは０．１～０．５］のうちの少なくとも１種類であることを特徴とする請求項１に記載の固体電解質電池。

【請求項４】　前記活物質および固体電解質の粒子を非晶質の酸化物で結着したことを特徴とする請求項１に記載の固体電解質電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は固体電解質電池に関し、特に、リチウムイオンの可逆的な吸蔵放出が可能な酸化物を活物質とする正極および負極との間に、リチウムイオン伝導性を有する結晶質酸化物からなる固体電解質を挟持する固体電解質電池に関する。

【０００２】

【従来の技術および発明が解決しようとする課題】近年の移動体通信の驚異的発展に伴い、移動体通信機器の電源として、小型でエネルギー密度が高いリチウム二次電池の需要が急増している。

【０００３】さらに、リチウム二次電池のエネルギー密度が高いことから、電気自動車等に使用される大型の電池に適用することも検討されている。

【０００４】しかしながら、リチウム二次電池も他の電池と同様に電解液を使用していることから、電池に関するトラブルの最大の要因である漏液が懸念される。特に、リチウム二次電池では可燃性の有機電解液を使用することから、安全性の面で不安がある。

【０００５】そこで有機電解液の代わりに固体電解質を用いる試みが多数なされている。固体電解質の一つに、ポリエチレンオキサイドのような高分子に$LiClO_4$

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などのリチウム塩を溶解させた高分子固体電解質がある。

【０００６】しかしながら高分子固体電解質は、室温ではセグメントの運動が遅いために、高分子バルク中でのイオン伝導度が低いこと、および高分子固体電解質と電極活物質との界面抵抗が大きいことから、実用に供せられるレベルのものは現れていないのが現状である。

【０００７】高分子固体電解質と電極活物質との界面抵抗を低減させるための方法もいくつか提案されている。例えば特開平８－１１１２３３号公報では、活物質の粒子表面にポリエチレンオキサイドやポリプロピレンオキサイドのようなポリエーテル、ポリフェニレンスルフィドチオエーテルのようなポリチオエーテル、またはポリアクリレートの主鎖の両端または一端を化学結合させたものを用いることを提案している。

【０００８】この方法によれば、活物質の表面にポリエーテル、ポリチオエーテルまたはポリアクリレートが化学結合しているため、活物質とポリエーテル、ポリチオエーテルまたはポリアクリレートを単に混合した場合に比べて、リチウムイオンが活物質表面から抜けていきやすく、また活物質表面に到達しやすくなる。したがって界面抵抗が低減できるという利点がある。さらに充放電に伴う活物質の体積変化があっても、活物質とポリエーテル、ポリチオエーテルまたはポリアクリレートが化学結合しているため、両者の接触が悪くなることはない。したがって界面抵抗が増加するのを抑制できるという利点がある。

【０００９】しかしながら、この方法では活物質表面にポリエーテル、ポリチオエーテルまたはポリアクリレートを結合させるのに１２０℃で３時間環流するという煩雑な操作が必要であり、量産する上では大量の活物質を処理しなければならないため製造コストが高くなるという欠点がある。また、ポリエーテル、ポリチオエーテルまたはポリアクリレートの未反応部分が酸化材である活物質と副反応を起こして充放電反応を阻害するという欠点がある。また、１２０℃で環流するという条件の下では副反応も起こりやすくなるため、再現性の良い結果が得られにくい。

【００１０】高分子の未反応部分と活物質との好ましくない副反応を抑制するために、特開平９－９７６１６号公報では、酸化チタンなどの充填剤を含有させた状態で重合させることを提案している。この方法によれば、酸化チタンが高分子の重合反応に対して選択的触媒となるために、活物質との副反応も起こりにくく、したがって充放電反応も阻害されにくいという利点がある。

【００１１】しかしながらこの方法は活物質と固体電解質との反応を抑えるものであるから、活物質と固体電解質との界面抵抗を低減させるために両者の間に化学結合を導入する場合には適用できない。したがって劣化は防げるものの、初期の抵抗が高いことに関しては何ら改善

できていない。

【００１２】このように高分子固体電解質と活物質との間に好ましくない副反応が起こるため、高分子の一部を活物質と化学結合させて界面抵抗を低減するのは困難である。

【００１３】また、高分子固体電解質が室温におけるセグメントの運動が遅いために、高分子バルク中でのイオン伝導度が低いという問題を解決する有効な手段は未だ現れていない。

【００１４】一方、室温でのイオン伝導度が10^{-4}～10^{-3} S／ｃｍと有機電解液に匹敵するレベルにある固体電解質もいくつか検討されている。そのような固体電解質としては、例えば非晶質硫化物が挙げられる。しかしながら非晶質硫化物は化学的に不安定であり、これを用いた固体電解質電池は実用化に至っていない。

【００１５】化学的に安定な無機酸化物において、室温でのイオン伝導度が10^{-4}～10^{-3} S／ｃｍと有機電解液に匹敵するレベルにある固体電解質もいくつか検討されている。そのような固体電解質としては、例えば$Li_{1+x}M_xTi_{2-x}(PO_4)_3$［MはＡｌまたはＧａ］であらわされるリチウムイオン伝導性結晶質酸化物がある。このようなリチウムイオン伝導性結晶質酸化物は通称ＬＩＳＩＣＯＮと呼ばれ、その組成や合成条件が多くの研究者により研究されている。

【００１６】しかしながら結晶質酸化物は、同じく結晶質である活物質との接触が点接触になるため、粒子間のイオン伝導に対する抵抗が高く、実用に供せられるレベルの固体電解質電池は未だ現れていないのが現状である。

【００１７】そこで、本発明者等は鋭意研究の結果、結晶質の活物質および固体電解質の粒子を非晶質の酸化物で結着することにより、室温で動作し得る固体電解質電池となることを見出した。非晶質の酸化物がリチウムイオン伝導に必要なホッピングサイトを提供するものと考えられる。

【００１８】しかしながら、非晶質の酸化物で結着した固体電解質電池も、内部抵抗が高く、活物質の利用効率が悪いという問題があった。

【００１９】本発明者等は、この原因が非晶質の酸化物と活物質との接触、および非晶質の酸化物と固体電解質との接触が、分子レベル・原子レベルにおいては不十分であることに起因するものと推測し、リチウムイオン伝導に必要なホッピングサイトを活物質および固体電解質のごく近傍に存在させるための手段を検討し、本発明に至った。

【００２０】

【課題を解決するための手段】上記課題を解決するために、本発明に係る固体電解質電池によれば、リチウムイオンの可逆的な吸蔵放出が可能な酸化物を活物質とする正極および負極との間に固体電解質を挟持する固体電解

質電池において、前記活物質および固体電解質の粒子は、その粒子表面に非晶質のシリカが化学結合したものであることを特徴とする。

【００２１】上記固体電解質電池では、前記活物質がスピネル型リチウムマンガン複合酸化物、スピネル型リチウムマグネシウムマンガン複合酸化物、スピネル型リチウムニッケルマンガン複合酸化物、スピネル型リチウムチタン複合酸化物、スピネル型リチウムニオブチタン複合酸化物、およびスピネル型リチウム鉄チタン複合酸化物のうちの少なくとも１種類であることが望ましい。

【００２２】また、上記固体電解質電池では、前記固体電解質が、$Li_{1+x}M_xTi_{2-x}(PO_4)_3$［MはＡｌまたはＧａ］、$Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$［MはＡｌまたはＧａ］、$Li_{1+(4-n)x}M_xTi_{2-x}(PO_4)_3$［Mは１価または２価の陽イオン、Mが１価のときｎ＝１、Mが２価のときｎ＝２、ｘは０．１～０．５］のうちの少なくとも１種類であることが望ましい。

【００２３】さらに、上記固体電解質電池では、前記活物質および固体電解質の粒子を非晶質の酸化物で結着したものであることが望ましい。

【００２４】

【発明の実施の形態】以下、本発明の実施形態を説明する。図１は本発明の固体電解質電池の構成例を示す断面図であり、１は正極缶、２は正極集電層、３は正極、４は絶縁部、５は固体電解質、６は負極、７は負極集電層、８は負極缶である。

【００２５】正極３および負極６に用いる活物質としては、スピネル型リチウムマンガン複合酸化物、スピネル型リチウムマグネシウムマンガン複合酸化物、スピネル型リチウムニッケルマンガン複合酸化物、スピネル型リチウムチタン複合酸化物、スピネル型リチウムニオブチタン複合酸化物、およびスピネル型リチウム鉄チタン複合酸化物のうちの少なくとも１種類が用いられる。これらはリチウムイオンのチャネルが３次元構造をとるため異方性が無く、したがって結晶のどの面が固体電解質と接していようとリチウムイオンの脱挿入に影響はないことから、固体電解質電池に用いられる活物質としてふさわしい。またこれら活物質は充放電に伴う体積変化が小さく、したがって充放電に伴う結晶崩壊が起こりにくいため、固体電解質電池に用いられる活物質としてふさわしい。

【００２６】これら活物質の粒子表面の結合水や吸着水を用いて、テトラアルコキシシラン等のシリカ原料を結合させ、さらにシリカ原料を重合させることで、非晶質のシリカが化学結合した活物質粒子を得ることができる。活物質の粒子表面へのシリカ原料の結合とシリカ原料同士の重合は室温で撹拌するだけで可能であり、環流などの煩雑な操作を伴わない。なお、反応を促進するために、触媒としてごく微量の水や酸を加えてもかまわない。このようにして活物質の粒子表面に非晶質のシリカ

を化学結合させることにより、リチウムイオンのホッピングサイトとなる酸化物イオンが活物質の粒子表面のごく近傍にまで存在しているため、未処理の活物質に比べてリチウムイオンが活物質表面から抜けていきやすく、またリチウムイオンが活物質表面に到達しやすくなる。したがって活物質粒子と非晶質酸化物との界面抵抗が低減できる。また充放電に伴う活物質の体積変化があっても、活物質と非晶質のシリカが化学結合しているため、両者の接触が悪くなることはない。したがって界面抵抗が増加するのを抑制できる。さらに活物質とシリカ原料との反応は脱水反応のみであり、充放電反応を阻害する他の副反応は起こり得ない。加えて、後述するように電池を形成する際に５００℃以上で熱処理を行なうため、脱水反応はほぼ完全に終了しており、生成した水が充放電反応を阻害することはない。

【００２７】正極３および負極６を作製するには、（１）非晶質のシリカを化学結合させた活物質と非晶質酸化物と成形助剤とを混合して、水または有機溶剤に分散させてスラリーを調整し、このスラリーを基材フィルム上に塗布して乾燥した後、裁断したものを５００～８００℃で熱処理する方法、（２）非晶質のシリカを化学結合させた活物質と非晶質酸化物とを、直接あるいは成形助剤を加えて造粒して金型に投入し、プレス機で加圧成形した後、５００～８００℃で熱処理する方法、（３）造粒した混合物をロールプレス機で加圧成形してシート状に加工した後、そのシートを裁断して５００～８００℃で熱処理する方法などが用いられる。

【００２８】ここで使用可能な成形助剤としては、例えばポリアクリル酸、カルボキシメチルセルロース、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラールなどの１種もしくは２種以上の混合物が挙げられる。

【００２９】基材フィルムとしては、例えばポリエチレンテレフタラートなどの樹脂フィルムが使用可能である。

【００３０】固体電解質５に用いられるリチウムイオン伝導性結晶質粒子としては、$Li_{1+x}M_xTi_{2-x}(PO_4)_3$［ＭはＡｌまたはＧａ］、$Li_{1+x+y}M_xTi_{2-x}Si_yP_{3-y}O_{12}$［ＭはＡｌまたはＧａ］、$Li_{1+(4-n)x}M_xTi_{2-x}(PO_4)_3$［Ｍは１価または２価の陽イオン、Ｍが１価のときｎ＝１、Ｍが２価のときｎ＝２、ｘは０．１～０．５］のうちの少なくとも１種類が用いられる。

【００３１】これら固体電解質の粒子表面の結合水や吸着水を用いて、テトラアルコキシシラン等のシリカ原料を結合させ、さらにシリカ原料を重合させることで、非晶質のシリカが化学結合した固体電解質の粒子を得ることができる。固体電解質の粒子表面へのシリカ原料の結合とシリカ原料同士の重合は室温で攪拌するだけで可能であり、環流などの煩雑な操作を伴わない。なお、反応を促進するために触媒としてごく微量の水や酸を加えてもかまわない。このようにして固体電解質の粒子表面に非晶質のシリカを化学結合させることにより、リチウムイオンのホッピングサイトとなる酸化物イオンが固体電解質の粒子表面のごく近傍にまで存在しているため、未処理の固体電解質に比べてリチウムイオンが固体電解質表面から抜けていきやすく、またリチウムイオンが固体電解質表面に到達しやすくなる。したがって界面抵抗が低減できる。さらに固体電解質とシリカ原料との反応は脱水反応のみであり、充放電反応を阻害する他の副反応は起こり得ない。加えて、後述するように電池を形成する際に５００℃以上で熱処理を行なうため脱水反応はほぼ完全に終了しており、生成した水が充放電反応を阻害することはない。

【００３２】固体電解質５を作製するには、（１）非晶質のシリカを化学結合させた固体電解質の粒子と非晶質酸化物と成形助剤とを混合して、水または有機溶剤に分散させてスラリーを調整し、このスラリーを基材フィルム上に塗布して乾燥した後、裁断したものを５００～８００℃で熱処理する方法、（２）非晶質のシリカを化学結合させた固体電解質の粒子と非晶質酸化物とを、直接あるいは成形助剤を加えて造粒して金型に投入し、プレス機で加圧成形した後、５００～８００℃で熱処理する方法、（３）造粒した混合物をロールプレス機で加圧成形してシート状に加工した後、そのシートを裁断して５００～８００℃で熱処理する方法などが用いられる。

【００３３】ここで使用可能な成形助剤としては、例えばポリアクリル酸、カルボキシメチルセルロース、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラールなどの１種もしくは２種以上の混合物が挙げられる。

【００３４】基材フィルムとしては、例えばポリエチレンテレフタラートなどの樹脂フィルムが使用可能である。

【００３５】活物質やリチウムイオン伝導性結晶質粒子を結着するのに用いられる非晶質酸化物としては、例えば、$40Li_2O-35B_2O_3-25LiNbO_3$、$30LiI-41Li_2O-29P_2O_5$などを挙げることができる。

【００３６】正極集電層２および負極集電層７は、正極缶１と正極３、あるいは、負極缶８と負極６との接触と集電のために配置され、例えば正極３および負極６上にスパッタリングによって形成された金、銀、銅、白金、パラジウム、ニッケルなどからなる。

【００３７】正極缶１および負極缶８は大気中の水分により充放電反応が阻害されるのを防ぐため、および正極３および負極６のそれぞれの端子として用いるために配置され、例えばアルミニウム、銅、ニッケル、ステンレススチール、チタンなどの金属の薄板が用いられる。

【００３８】絶縁部４は正極３と負極６との短絡を防ぐ

ために配置され、例えばポリエチレン、ポリプロピレン、ポリイミドなどの高分子が用いられる。

【００３９】

【実施例１】$Li_{1.1}Mn_{1.9}O_4$を１００ｗｔ％、テトラメトキシシランを５０ｗｔ％秤量し、室温にて２時間攪拌した後１２０℃で２時間乾燥することにより、非晶質のシリカを化学結合させた$Li_{1.1}Mn_{1.9}O_4$を得た。

【００４０】非晶質のシリカを化学結合させた$Li_{1.1}Mn_{1.9}O_4$を９５ｗｔ％、$40Li_2O-35B_2O_3-25LiNbO_3$を５ｗｔ％秤量し、これにポリブチラールを５ｗｔ％、イソプロピルアルコールを２５ｗｔ％加えて、遊星型ボールミルで３０分攪拌しスラリーを調整した。

【００４１】このスラリーを用いてドクターブレード法により正極テープおよび負極テープを作製した。なお、負極においては$Li_{1.1}Mn_{1.9}O_4$の３Ｖ充放電領域を使用するものである。

【００４２】次に$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$を１００ｗｔ％、テトラメトキシシランを５０ｗｔ％秤量し、室温にて２時間攪拌した後１２０℃で２時間乾燥することにより、非晶質のシリカを化学結合させた$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$を得た。

【００４３】非晶質のシリカを化学結合させた$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$を９０ｗｔ％、$40Li_2O-35B_2O_3-25LiNbO_3$を１０ｗｔ％秤量し、これにポリブチラールを５ｗｔ％、イソプロピルアルコールを２５ｗｔ％加えて、遊星型ボールミルで３０分攪拌しスラリーを調整した。

【００４４】このスラリーを用いてドクターブレード法により固体電解質テープを成形した。

【００４５】正極テープ、固体電解質テープ、負極テープを積層し、圧着した後、６５０℃で３時間熱処理した。熱処理後のサイズは３０×３０ｍｍで、厚さは正極が１００μｍ、固体電解質が１０μｍ、負極が１００μｍの、計２１０μｍであった。

【００４６】正極側および負極側に金をスパッタリングして集電層を形成した後、内側３１×３１ｍｍ、外側３５×３５ｍｍのポリエチレン枠にはめ込み、二枚のアルミニウム板に挟んで熱圧着することで固体電解質電池を作製した。

【００４７】

【実施例２】$Li_{1.1}Mn_{1.9}O_4$を１００ｗｔ％、テトラメトキシシランを５０ｗｔ％秤量し、室温にて２時間攪拌した後１２０℃で２時間乾燥することにより、非晶質のシリカを化学結合させた$Li_{1.1}Mn_{1.9}O_4$を得た。

【００４８】非晶質シリカを化学結合させた$Li_{1.1}Mn_{1.9}O_4$を９５ｗｔ％、$40Li_2O-35B_2O_3-25LiNbO_3$を５ｗｔ％秤量し、これにポリブチラールを５ｗｔ％、イソプロピルアルコールを２５ｗｔ％加えて、遊星型ボールミルで３０分攪拌しスラリーを調整した。このスラリーを用いてドクターブレード法により正極テープを作製した。

【００４９】次に、$Li_{1.33}Ti_{1.67}O_4$を１００ｗｔ％、テトラメトキシシランを５０ｗｔ％秤量し、ＵＶを照射しながら室温にて２時間攪拌した後１２０℃で２時間乾燥することにより、非晶質のシリカを化学結合させた$Li_{1.33}Ti_{1.67}O_4$を得た。

【００５０】非晶質シリカを化学結合させた$Li_{1.33}Ti_{1.67}O_4$を９５ｗｔ％、$40Li_2O-35B_2O_3-25LiNbO_3$を５ｗｔ％秤量し、これにポリブチラールを５ｗｔ％、イソプロピルアルコールを２５ｗｔ％加えて、遊星型ボールミルで３０分攪拌しスラリーを調整した。このスラリーを用いてドクターブレード法により負極テープを作製した。

【００５１】次に$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$を１００ｗｔ％、テトラメトキシシランを５０ｗｔ％秤量し、室温にて２時間攪拌した後１２０℃で２時間乾燥することにより、非晶質のシリカを化学結合させた$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$を得た。

【００５２】非晶質のシリカを化学結合させた$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$を９０ｗｔ％、$40Li_2O-35B_2O_3-25LiNbO_3$を１０ｗｔ％秤量し、これにポリブチラールを５ｗｔ％、イソプロピルアルコールを２５ｗｔ％加えて、遊星型ボールミルで３０分攪拌しスラリーを調整した。このスラリーを用いてドクターブレード法により固体電解質テープを成形した。

【００５３】正極テープ、固体電解質テープ、負極テープを積層し、圧着した後、６５０℃で３時間熱処理した。熱処理後のサイズは３０×３０ｍｍで、厚さは正極が１００μｍ、固体電解質が１０μｍ、負極が１００μｍの、計２１０μｍであった。

【００５４】正極側および負極側に金をスパッタリングして集電層を形成した後、内側３１×３１ｍｍ、外側３５×３５ｍｍのポリエチレン枠にはめ込み、二枚のアルミニウム板に挟んで熱圧着することで固体電解質電池を作製した。

【００５５】

【比較例１】活物質および固体電解質の粒子をテトラメトキシシランで処理していないことを除けば、実施例１と同じ方法で固体電解質電池を作製した。

【００５６】

【比較例２】活物質および固体電解質の粒子をテトラメトキシシランで処理していないことを除けば、実施例２と同じ方法で固体電解質電池を作製した。

【００５７】

【電気化学的評価】以上の固体電解質電池を用いて、１００μＡ／cm^2の電流密度で充放電容量の測定を行った。その結果を表１に示す。

【００５８】

＊　＊【表１】

試　料	充電容量 (mAh／g)	放電容量 (mAh／g)	充放電効率 (%)
実施例１	１０５	９１	８７
実施例２	９９	８６	８７
比較例１	８０	３６	４５
比較例２	８２	４０	４９

【００５９】表１からわかるように、テトラメトキシシランで処理して非晶質のシリカを化学結合させた活物質および固体電解質の粒子を用いた実施例１、２では、未処理の活物質および固体電解質の粒子を用いた比較例１、２に比べて初期の充電容量が高く、充放電効率が高い。

【００６０】これは、活物質および固体電解質の粒子表面に非晶質のシリカが化学結合したことにより、リチウムイオンのホッピングサイトとなる酸化物イオンが活物質および固体電解質の粒子表面のごく近傍にまで存在しているため、未処理の活物質および固体電解質の粒子に比べて界面抵抗が低減できたためと推測される。

【００６１】

【発明の効果】以上のように、本発明に係る固体電解質電池によれば、リチウムイオンの可逆的な吸蔵放出が可能な酸化物を活物質とする正極および負極との間に、リチウムイオン伝導性を有する結晶質酸化物からなる固体電解質を挟持する固体電解質電池において、上記活物質および固体電解質の粒子がその粒子表面に非晶質のシリカが化学結合したものであることから、リチウムイオンのホッピングサイトとなる酸化物イオンが活物質および固体電解質の粒子表面のごく近傍にまで存在しているた※※め、未処理の活物質および固体電解質の粒子に比べて界面抵抗が低減され、活物質の利用効率が高い固体電解質電池を得ることができる。

【００６２】また充放電に伴う活物質の体積変化があっても、活物質と非晶質のシリカが化学結合しているため、両者の接触が悪くなることはない。したがって界面抵抗が増加するのを抑制できる。これにより初期の充放電効率が向上する。

【００６３】さらに、活物質または固体電解質とシリカ原料との反応は脱水反応のみであり、充放電反応を阻害する他の副反応は起こり得ない。したがって再現性の良い結果を得ることができる。

【００６４】加えて、電池を形成する際に５００℃以上で熱処理を行なうため脱水反応はほぼ完全に終了し、生成した水が充放電反応を阻害することはない。

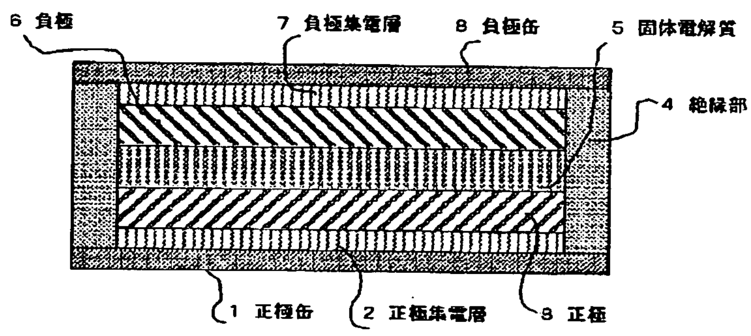
【図面の簡単な説明】

【図１】本発明に係る固体電解質電池の構成例を示す断面図である。

【符号の説明】

１：正極缶、２：正極集電層、３：正極、４：絶縁部、５：固体電解質、６：負極、７：負極集電層、８：負極缶

【図１】



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